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November 22, 1995

95-RF-08787

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HYDROGEN GAS GENERATION AND ACCUMULATION IN SOLUTION TANKS - VM-156-95

Ref: Unreviewed Safety Question Determination (USQD), USQD-RFP-95.0387-CAS

PURPOSE

This correspondence provides a revised USQD for radiolytic hydrogen gas generation in actinide tanks in Buildings 371 and 771.

DISCUSSION

In response to DOE, RFFO comments, the Unreviewed Safety Question (USQ) for radiolytic hydrogen gas generation in actinide solution tanks in Buildings 371 and 771 has been revised.

This revision indicates the application and use of compensatory measures to address immediate worker safety. The earlier version of the USQD (referenced above) had a "NO" answer to this USQD question (question #13).

RESPONSE

If you have any questions or comments, please contact G. A. Zimmerman of Nuclear Safety at extension 8264 or pager 7368.

*R E Kell*  
Vik Mani, Vice President  
Safety Engineering & Technical Services

RAR:la

Orig. and 1 cc - D. A. Brockman

Attachment:

1. USQD-RFP-95.1051-CAS, Gaseous Hydrogen Generation and Accumulation in Solution Tanks in Buildings 371 and 771.

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## USQD COVER SHEET

USQD No. USQD-RFP-95.1051-CASBuilding #      Page 1  
RFP of 8Title GASEOUS HYDROGEN GENERATION AND ACCUMULATION IN  
SOLUTION TANKS IN BUILDINGS 371 AND 771.Job # 381364-H2

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Note 1

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Note 8

Revision No.

Note 9

New Evaluation Required

Yes

No

- Note 1: If the CSR is needed for revision, then CSR initials, otherwise CEV marks N/A and initials.  
 Note 2: The Certified Evaluator initials for revision of USQD.  
 Note 3: Peer Reviewer initials for revision of USQD.  
 Note 4: Program Manager, NS initials for revision.  
 Note 5: ORC initials for revision.  
 Note 6: Responsible Manager initials for revision.  
 Note 7: Operations Manager initials for revision.  
 Note 8: Revision of the USQD.  
 Note 9: Check (✓) if revision significant to require reevaluation. Initials above needed to confirm only No determinations and a justification is required.  
 Note 10: Changes to this USQD shall be made by a Certified Evaluator.  
 Note 11: Mark not applicable signature blanks "N/A".



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**UNREVIEWED SAFETY QUESTION DETERMINATION**  
**USQD Number: USQD-RFP-95.1051-CAS**

**USQD Title:** Gaseous Hydrogen Generation and Accumulation in Solution Tanks in Buildings 371 and 771.

**Description and Purpose of Proposed Activity:** This evaluation supersedes the previous analysis addressing the hydrogen in tanks issue (USQD-RFP-95.0387-CAS), but changes that analysis only in that the compensatory actions associated with this issue are referenced and discussed.

The unanticipated curtailment of operations in plutonium processing facilities at RFETS has resulted in long term storage of a significant volume of actinide solutions. These solutions are primarily stored in tanks which, due to the long period of storage, ultimately have become susceptible to buildup of radiolytic gases (The issue of radiolytic gas buildup in drums and bottles has been separately addressed in USQD-RFP-95.0180). The principal gaseous products from alpha radiolysis of the acid based actinide solutions contained in these tanks are hydrogen and oxygen. The hazards associated with generation and buildup of radiolytic gases over stored actinide solutions was not considered in the original safety analysis for the respective facilities. In recognition of the various hazards associated with long term actinide solution storage, a study of these hazards was commissioned by RFETS and performed by LATO<sup>4</sup>. Among LATO's conclusions in this study was that radiolytic gas generation and accumulation does not represent an undue hazard if tanks containing actinide solutions have been properly vented during the course of operational curtailment.

Subsequent to the LATO study, the referenced transmittal<sup>1</sup> directed the investigation of vent status of tanks susceptible to significant hydrogen accumulation. The course of this investigation<sup>3</sup> involved the development and implementation of calculational methodology to predict rates and overall accumulation of hydrogen in a population of potentially susceptible tanks consistent with empirically derived rates of radiolytic gas generation<sup>2</sup>. Conducted under an initial conservative assumption that the tanks were not vented, the calculation<sup>3</sup> was used to identify those tanks which if not vented, could represent a significant explosion hazard and also to delineate those tanks whose potential for hydrogen accumulation was below a reasonable level of concern. (Significant in this context is assumed to be that quantity of hydrogen that if ignited or detonated could compromise the integrity of the respective tank.) A screening criterion was established to differentiate the tanks of lesser concern from tanks susceptible to significant buildup of hydrogen. The criterion selected is hydrogen accumulation which has an explosive yield equivalent to 200g of TNT. The basis for this criterion is that it represents a conservative level of explosive force at or below which, it was presumed, the potential for tank rupture is small. For those tanks which have the potential for greater hydrogen accumulation, a determination of the maximum blast effects outside a given tank were determined assuming that detonation of the contained hydrogen causes a loss of tank containment.

The initial calculations indicated that high level (>100 g/l) solutions produced gases at rates high enough to represent an unacceptable hazard if the radiolytic gases were not vented. A verification of venting of these tanks, and the balance of susceptible tanks in Building 771 was subsequently performed<sup>4</sup>. Such verification could not be performed on the susceptible tanks in Building 371 due to inaccessibility, so the calculation was used to predict hydrogen inventories to a point in time two years hence, assuming no venting of the tanks.

As a result of the high energy of activation necessary to cause direct detonation of stoichiometric hydrogen/oxygen mixtures contained in a tank<sup>9</sup>, it is assumed that spontaneous detonation is an incredible event. Ignition of the gas is contingent upon the presence of an ignition source and can result only in a pressure rise of  $\leq 150$  psig<sup>8</sup>. Despite the fact that LATO<sup>4</sup> could not identify an ignition source for contained hydrogen, ongoing activities in the building (maintenance involving welding, grinding, etc.) necessitate consideration of possible ignition of the contained hydrogen and the potential for subsequent detonation. If ignition of the gas in a tank and the subsequent deflagration of the explosive mixture is a credible event, the potential for detonation following ignition cannot be ruled out.

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This case is particularly identifiable for tanks with internal structures (interior drain and fill lines, etc.) or obstructions such as Raschig rings<sup>9</sup>. It can be reasonably assumed that if ignition takes place geometrical considerations would dictate that the potential for detonation in annular tanks is low whereas Raschig ring tanks must be assumed to detonate at some credible frequency. Qualitatively, due to the lack of identified ignition sources and the improbability of detonation, tank explosion due to hydrogen would be aptly ascribed the frequency consistent with a PC-4 event.

Two potential accident types result from the presence of the hydrogen hazard. The first and least consequential type is the ignition and deflagration of the gas contained in the tank. As discussed above, the pressure rise due to deflagration is limited and does not represent a compromise to tank integrity, but would likely result in high energy leakage (spills) at piping connections and/or valve components. The second accident is the detonation of the gas following ignition and deflagration.

The determination of blast effects inside a contained vessel (such as a solution tank) are very complex and difficult to predict in any generic sense. The magnitude of the blast wave can be approximated<sup>8</sup> as 20 times the static pressure for some systems. This approximation may not be accurate in certain tanks due to the potential blast wave flame acceleration mechanisms that may occur (as in Raschig ring tanks). It is also extremely difficult to ascribe a yield factor for hydrogen in an enclosed space due to the uncertainty in the mechanism and rate of hydrogen detonation in an obstructed, enclosed space. Additionally, the material condition of the tanks and their effective design pressures are not easily determined. Therefore, for the purpose of this analysis, it is assumed that the blast pressure in the susceptible tanks is capable of breaching the containment of the tank and that the magnitude of the explosion inside the tank is commensurate with a yield factor of 1.0. Once the explosion escapes the containment of the tank it then propagates as an unconfined vapor cloud explosion<sup>8</sup>. A yield factor of 0.03<sup>8</sup> can be used to determine the explosive capability of hydrogen in such an explosion propagation. As a conservative approximation in this analysis, deflagration outside a ruptured tank is assumed to carry the full force of the explosive contents of the tank. (i.e. No energy is expended in the explosion in the process of rupturing the tank.)

## Reference Documents:

1. Transmittal ltr #LRT:GWS:12265, dtd. 23 Dec. 1994; Vent Status of Tanks that Potentially Generate Hydrogen.
2. A.R. Kazanjian and D.R. Horrel, 'Radiolytically Generated Gases in Plutonium-Nitric Acid Solutions,' *Radiation Effects*, 13, 1972.
3. Nuclear Safety Calculation #CALC-RFP-95.0386-RGC-USQD.
4. R.L. Ames et. al, 'Plutonium and Uranium Solutions Safety Study,' LATO Report # LA-UR-93-3282, October 1993.
5. EG&G Rocky Flats Interoffice Correspondence, 'Potential for Line Blockage Resulting in Hydrogen Pressurization of Actinide Solution Holding Tanks in Building 771'. Correspondence #ABA-001-95.
6. Building 771 FSAR, June 1987.
7. Building 371 FSAR, Revised July, 1981.
8. Handbook of Chemical Hazard Analysis Procedures, FEMA, US DOT, US EPA handbook, Federal Emergency Management Agency Publications Office, Washington D.C., 1989.

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9. W.E. Baker and M.J. Tang, *Gas, Dust and Hybrid Explosions*, Elsevier, New York, 1991.
10. Evaluation of Unreviewed Safety Questions, RFETS Procedure 3-J69-NSPM-5C-01, Aug. 31, 1994.
11. Occurrence Report Number: RFO-EGGR-771OPS-1995-0064, Dated 3-1-95.
12. NFPA 69, *Standard on Explosion Prevention Systems*, National Fire Protection Association, Quincy, MA, 1992.

**Applicable Requirements:** There are no OSR requirements that are specifically applicable to radiolytic hydrogen generation or accumulation. The process tanks in which quantities of hydrogen could exist are not described in the facility FSARs and there are no OSR requirements associated with these tanks.

**Safety, Operating Function, and Operating Conditions Identification:** As identified above, the solution tanks affected by potential hydrogen buildup are not specifically or implicitly described or considered in the FSAR facility description, operating safety requirements or accident analyses. These tanks are considered to be configured and utilized for process functions which may be monitored and/or controlled by vital safety systems in the facility but do not directly impact the function of vital systems.

**Failure Mode, Hazard, and Accident Identification:** Radiolytically generated hydrogen that accumulates to explosive levels in process tanks potentially represents a potential overpressurization or explosive hazard, the implications for which not having been previously evaluated in the facility safety analyses. The Building 771 FSAR does, however, identify metal/water (calcium metal and water) reaction(s) as a potential source of hydrogen. The accident analyses also evaluate the risk implications from several other explosion sources. The present analysis concludes that the potential radiolytic hydrogen risk is bounded by existing explosion and spill scenarios identified in the present safety analyses.

**Unreviewed Safety Question Determination Questions:**

1. Could the proposed activity increase the probability of occurrence of an accident previously evaluated in a Safety Analysis? Yes ☐ No ☒ Explain: Accumulation of radiolytic hydrogen gas and subsequent explosion is an accident of a different type not previously analyzed in the Safety Analysis.

The presence of explosive levels of hydrogen in process tanks represents a new explosion source not previously considered in the facility accident analyses. The frequency of this potential accident is however quite small owing to the inability to identify and ignition source<sup>4</sup>. Since the gas evolution rate, even in the highly productive tanks, is insufficient to create a flammable mixture at the vent exit; the only potential source for ignition of this gas would be the inadvertent breach of the vent header or tank(s) by a high energy source (e.g. welding or grinding). Once ignited, the probability of detonation occurring is less than one. The combination of these factors reduces the probability of tank explosion to the point that it is within the PC-4 frequency range identified in Appendix 2 of Reference 10. While this potential source of explosion increases the overall frequency of explosion evaluated in the safety analyses, its frequency is bounded by the FSAR limiting accidents and does not *significantly* increase the overall frequency of explosion for either facility.

The presence of small quantities of hydrogen does not represent an unacceptable explosive hazard nor, based upon the frequency of initiation, does the potential for ignition of these quantities of hydrogen represent an increase in spill frequency (from tank and related system pressurization) in the susceptible facilities beyond the preponderance of spill scenarios currently

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evaluated.

2. Could the proposed activity increase the consequences of an accident previously evaluated in a Safety Analysis? Yes ☐ No ☒ Explain: Accumulation of radiolytic hydrogen gas and subsequent explosion is an accident of a different type not previously analyzed in the Safety Analysis.

Chapter 8 of the Building 771 FSAR discusses several explosion related accidents. These accidents are associated with explosive materials with TNT equivalents of up to 2,000g. The consequences (MOI) associated with a tank explosion (detonation) involving the entire contents of a given tank exceed the consequences identified for any of the currently postulated explosions. The tanks in Building 771 have been proven to be vented<sup>6</sup> and the consequences have been shown<sup>3</sup> to be within the limits for PC-4 events as identified in Reference 10. These consequences compare favorably with the Building 771 limit of 1E-1 rem and the Building 371 MCA limit of 2E-1 rem.

The respective facility FSARs address numerous leakage scenarios. The leakage associated with deflagration of small quantities of explosive hydrogen mixtures in process tanks would be bounded by quantities released in other spill scenarios.

3. Could the proposed activity increase the probability of occurrence of a malfunction of equipment important to safety previously evaluated in Safety Analyses? Yes ☐ No ☒ Explain: The potential detonation of small quantities of hydrogen mixtures in process tanks will be largely contained by these tanks<sup>4</sup>. Detonation of hydrogen in these tanks would, at worst, result in flame deflagration outside the tanks consistent with TNT quantities of less than 20g<sup>3</sup> (assuming that none of the explosive energy is expended in the rupture of the tank). The accumulation of these quantities of hydrogen and the potential for detonation of these mixtures would therefore not have an impact on vital equipment in the vicinity. Vital system failure mechanisms currently postulated in the facility Safety Analyses will not be affected by the presence or detonation of the predicted quantities of hydrogen in process tanks.
4. Could the proposed activity increase the consequence of a malfunction of equipment important to safety previously evaluated in Safety Analyses? Yes ☐ No ☒ Explain: The accumulation and potential detonation of hydrogen would likely not be linked to a failure of vital system components. The malfunction of equipment would not increase the frequency of detonation of hydrogen contained in process tanks nor would the presence of this potential hazard impact the consequences of equipment malfunction(s). Similarly, no mechanism is evident that would link equipment malfunctions to ignition of contained hydrogen.
5. Could the proposed activity create the possibility of an accident of a different type than any previously evaluated in Safety Analyses? Yes ☒ No ☐ Explain: As discussed above, an explosion in a process tank due to accumulation of hydrogen gas or any other explosive source is not an accident that was considered in the safety analyses.

Verification that tanks which have the capability of producing large quantities of hydrogen are currently vented and will remain vented has been completed<sup>6</sup>. Venting limits the explosive capability of any gas accumulation to a level where detonation of hydrogen in any tank would not produce sufficient energy to significantly propagate such an explosion outside the containment of the respective tank. Such a detonation could and would likely result in a high energy release of the contained radionuclides with the associated risk of plutonium aerosol formation. The risk from such an occurrence is however, acceptable within the limits identified in Reference 10.

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While the offsite consequences of a potential hydrogen explosion are bounded by the existing safety analyses there are unevaluated worker safety issues that emerge resulting from the postulated scenario(s) associated with hydrogen detonation and tank rupture. Compensatory actions associated with this worker safety issue are discussed in Reference 11 and in response to question 13 below.

6. Could the proposed activity create the possibility of a malfunction of equipment important to safety of a different type than any previously evaluated in Safety Analyses? Yes \_\_\_ No X  
Explain: As discussed in #3 above, operability or operation of vital system components are not affected by the condition of accumulation of radiolytic hydrogen and would not be affected by detonation of the small quantities of hydrogen that have been projected<sup>3</sup> to be present in the tanks under consideration. The possibility of equipment malfunction is therefore not enhanced by the presence of this potential hazard.
7. Could the proposed activity reduce the margin of safety as defined in the basis for any TSR? Yes \_\_\_ No X Explain: As discussed above, the condition associated with the production and long term accumulation of hydrogen is not addressed in the OSRs for Buildings 371 or 771 and its presence does not impact assumptions in the bases with respect to the availability of vital equipment or their respective functions. Any margin of safety assumed in the OSR is therefore not compromised by the presence of radiolytic hydrogen within the limits assumed in the supporting calculation<sup>3</sup>.
8. Does the activity constitute a USQ? Yes X No \_\_\_ Explain: The answer to question 5 above is yes. Hydrogen accumulation in process tanks represents a previously unanalyzed accident and therefore constitutes an Unreviewed Safety Question.

NOTE 1 *If any of the above seven USQD questions are checked (✓) Yes, the activity is a USQ. The Program Manager, NS or Director, Engineering and Safety Services is immediately notified before proceeding.*

9. Does the activity require a change to the TSR (or OSR)? Yes \_\_\_ No X The issue of radiolytic hydrogen accumulation is not currently addressed in the building OSRs and a new OSR requirement is not required to maintain facility safety. The accumulation of small quantities of explosive hydrogen gas mixtures in tanks is bounded by existing analyses and does therefore not impact the existing facility safety envelope.
10. Could the activity result in exceeding the criticality safety acceptance criteria? Yes \_\_\_ No X Explain: The generation and accumulation of gaseous hydrogen does not impact criticality safety in the susceptible tanks. Potential detonation as well does not compromise criticality safety acceptance criteria in the tanks or if such detonation results in leakage (spillage) of liquid from the tanks and piping.

NOTE 2 *If any of the above questions are checked (✓) Yes, DOE approval is required to proceed.*

11. Does the proposed activity require an authorization basis related FSAR change? Yes \_\_\_ No X Since the potential consequences from the accumulation and potential detonation of hydrogen in process tanks are conditions and events which are bounded by events currently evaluated in the FSAR Safety Analyses, this condition does not require a change to the respective facility FSARs or other authorization basis documents.

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## UNREVIEWED SAFETY QUESTION DETERMINATION

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## 12. Hazardous Material Evaluation:

1. Does the proposed activity introduce a new hazardous material not evaluated in a Safety Analysis? Yes ☐ No ☒ Explain: The condition does not involve, incorporate, or authorize the introduction or use of hazardous material.
2. Does the activity increase the probability or consequences of an accident resulting from hazardous materials previously evaluated in Safety Analyses, or exceed any established inventory quantity limits? Yes ☐ No ☒ Explain: Since no hazardous materials are authorized, accidents associated with such materials are not facilitated by the presence of radiolytic hydrogen accumulation in process tanks.

**NOTE 3** *If Hazardous Material Evaluation has a question checked (✓) Yes, DOE notification is required to proceed with proposed activity.*

13. Are Compensatory Actions required? Yes ☒ No ☐

In order to mitigate the possibility of injury and/or contamination to facility workers, access to the areas surrounding the susceptible tanks has been precluded or minimized<sup>11</sup>. This limitation of access is to remain in effect until such time that a means is implemented to purge the gas spaces of the susceptible tanks to the extent necessary to reduce and maintain hydrogen concentrations in the tanks to a level at or below an established lower explosive limit<sup>12</sup>.

Once such a program has been implemented, it is anticipated that the restrictions associated with access to susceptible tank areas will be suspended.

## 14. USQD Conclusion

Several of the existing tanks in Building 771 and 371 have the capability to accumulate radiolytic hydrogen to the extent that this hydrogen would represent a significant hazard. All of the susceptible tanks in Building 771 however have been demonstrated to be vented<sup>6</sup> and the rates of hydrogen production in the susceptible Building 371 tanks is such that these tanks can remain unvented for an additional two(2) years from the time of this writing prior to these tanks representing a concern that will require re-evaluation<sup>3</sup>. (The 371 tanks are capable of accumulating hydrogen to pressures only slightly in excess of atmospheric pressure and the accumulated hydrogen inventories could, at worst, result in deflagrations outside ruptured tanks with TNT equivalents of less than 20g.)

Venting of susceptible tanks has been verified. Therefore the extent of any ignition of hydrogen would be limited to deflagrations and subsequent leakage from piping components and/or connections downstream from affected tanks or deflagrations outside tanks ruptured by detonation. The risk from this hazard is bounded by the existing Safety Analyses as defined in Reference 10. However, since this hazard has not been analyzed in the existing Authorization Basis and represents an undefined worker safety hazard, it does constitute an Unreviewed Safety Question (USQ).

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| .            | Current | <Dir>           | ..           | Parent  | <Dir>           |
|--------------|---------|-----------------|--------------|---------|-----------------|
| 771EOE-4.USQ | 103,328 | 12-16-94 07:17a | 93-1175 .R1  | 32,372  | 12-09-94 05:00p |
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| EOESAAM .COM | 4,614   | 03-14-95 05:33p | FORM .SES    | 53,451  | 09-29-94 03:25p |
| FORM .USQ    | 76,860  | 09-29-94 03:24p | H2COVER .USQ | 3,708   | 01-06-95 07:12a |
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| H2REFIND.771 | 18,492  | 01-23-95 09:04a | H2ROUGH .371 | 49,137  | 01-22-95 10:14a |
| H2ROUGH .771 | 50,827  | 01-23-95 05:24p | H2TABLE .    | 42,018  | 01-20-95 10:55a |
| NOSTYLE .USQ | 85,932  | 03-21-95 07:44a | SYNOPSIS.    | 32,126  | 01-09-95 03:24p |
| TANKDRN1.USQ | 112,781 | 04-14-95 09:58a | TANKPURG.USQ | 89,020  | 04-03-95 10:41a |